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COATINGS AND ENAMELS

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CHEMICAL STABILITY OF TITANIUM ENAMEL COATINGS

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Titanium enamel for steel cookware has been developed. The enamel contains less fluoride and anhydrous boron than ÉSP-117 commercial enamel. A comparative analysis of the chemical stability of enamel frits and coatings based on them is performed. The new enamel is chemically more stable than ÉSP-117 commercial enamel.

Key words: chemical stability, water resistance, crystallization, mathematical model.

Covering enamels used for enameled steel cookware must meet more stringent requirements for chemical stability. In addition, there are limits on the content of a number of components which can easily leach out of the coatings in hot water and water solutions of food reagents and can present a health hazard for humans.

Manufacturing experience shows that ÉSP-117 titanium-containing frit is most widely used for enameling the inner and outer surfaces of steel cookware. Other enamels can also be used for such purposes [1].

There are many works devoted to improving enamel compositions for steel cookware, for example, [2 – 4]. The objective of much work of this kind is to eliminate from enamel compositions any components that are harmful to the environment and humans, for example, fluorides and boron oxide. However, together with the drawbacks mentioned these components also have positive effects on a number of properties of enamel coatings. For this reason their complete elimination from enamels is not always justified. In practice, it is desirable to optimize the content of fluorides and anhydrous boron in enamels used for different purposes, specifically, in enamel coatings for steel cookware.

The objective of the present work is to develop titanium enamel with reduced fluoride and anhydrous boron contents and enhanced chemical stability compared with ÉSP-117 enamel.

The enamel composition was designed using linear programming and mathematical models that describe the dependence of the technological and operating properties of enamel glasses on their composition [5 – 8]. The final optimal composition of the titanium enamel is as follows (wt.%): 44 – 46 SiO_2; 12 – 14 B_2O_3; 1 – 2 P_2O_5; 21 – 23 (TiO_2 + ZrO_2 + Al_2O_3); 1 – 2 (CaO + MgO); 13 – 14 (Na_2O + K_2O) and 2.2 F^+ (parts by weight above 100). Compared with ÉSP-117 frit the new enamel composition differs by reduced content of fluorine, anhydrous boron and alkali oxides. In addition, zirconium dioxide was added to its composition.

For comparative studies, the enamel with the composition indicated was smelted under laboratory conditions and the properties of the glass frit and the coatings based on it were determined. The water resistance of the glass frit was determined by the standard procedure (GOST 10134.0–82 – 10134.3–82) and evaluated according to the amount of 0.01n HCl (cm^3/g) required to neutralize the alkali in the aqueous extract. The higher the water resistance of the frit, the less HCl is expended on titration of the aqueous extract. In addition, the effect of the interaction time of the reagent on frit leachability was investigated.

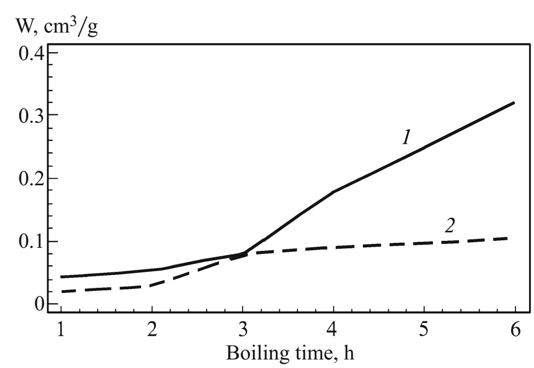

Fig. 1. Water resistance W of ÉSP-117 commercial frit (*1*) and the new OPT frit (*2*).

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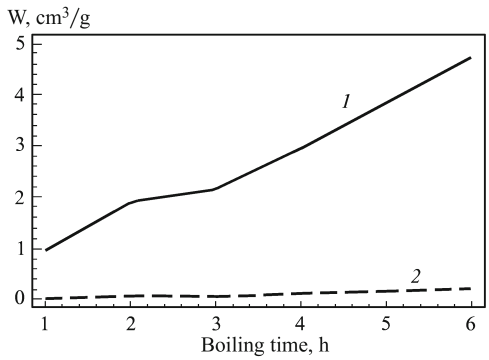

Fig. 2. Water resistance W of ÉPS-117 commercial frit (*1*) and the new OPT frit (*2*) after their crystallization.

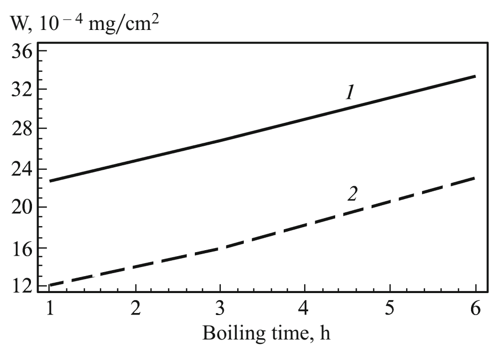

Fig. 3. Water resistance W of coatings based on ÉSP-117 commercial enamel frit (*1*) and the new OPT frit (*2*).

It follows from the data in Fig. 1 that the optimized composition of the titanium enamel is characterized by higher water resistance than the ÉSP-117 commercial enamel.

Since during sintering titanium enamels undergo crystallization with a crystalline phase of titanium dioxide being released, the water resistance of glass frits which underwent preliminary heat-treatment at 800°C was also determined.

The results are presented in Fig. 2 and show that the crystallization of ÉSP-117 frits substantially lowers its water resistance. The water resistance of the new enamel decreased very little, and the amount of alkali oxides passing into solution is practically independent of the testing time.

On this basis it can be supposed that the water resistance of enamel coatings is determined by, above all, the water resistance of the residual glass phase, which for ÉSP-117 enamel is less chemically stable than the new enamel. This is also confirmed by comparative studies of the water resistance of enamel coatings (Fig. 3), which were evaluated according to the amount of alkali oxides passing into the aqueous extracts (mg/cm^2). Here, it is observed that the new enamel is highly resistant to hot water and acetic acid (Table 1).

According to the data in Table 2 the new enamel frit makes it possible to obtain enamel coatings not only with enhanced chemical resistance but also with aesthetic-user properties no worse than those of coatings based on ÉSP-117 commercial frit.

TABLE 1. Chemical Stability of Coatings by the Spot Method for ÉSP-117 Commercial and New OPT Frits

Firing temperature, °C	Firing time, min	Changes to the coating surface after exposure to 4% acetic acid in time, min					
		ÉSP-117			OPT		
		10	20	30	10	20	30
860	6	+	+	+	+	+	+
	3	+	+	+	+	+	+
820	6	+	+	O	+	+	+
	3	+	O	O	+	+	+
780	6	+	O	O	+	+	+

Notations: +) no loss of surface luster; O) traces of acid effect observed with no loss of surface luster.

TABLE 2. Luster (KZO) and Whiteness (KDO) of Enamel Coatings

Firing temperature, °C	Firing time, min	KZO, %		KDO, %	
		ÉSP-117	OPT	ÉSP-117	OPT
860	6	69	75	83	85
	3	53	79	82	85
820	6	67	74	84	84
	3	72	84	84	81
780	6	73	75	83	82

In conclusion, on the basis of the results obtained the optimized titanium enamel can be used for enameled steel cookware.

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